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New trends in light scattering

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Abstract

In this article we review some of the most important new developments in light scattering that have emerged over the past 10 years. Some of the new methods substantially extend the range of accessible time and length scales. Different cross-correlation methods are now available to suppress multiple scattering over a large concentration range. Novel low coherent light sources on the other hand have stimulated progress in the field of heterodyne detection. Many of these new approaches take advantage of the nowadays available area detectors such as high resolution CCD/CMOS video cameras. This has enabled large scale parallel processing of speckle intensity fluctuations and in consequence has provided a wealth of possibilities in dynamic light scattering such as multi-speckle detection and time resolved correlation analysis.

1. Introduction

The success of light scattering is probably due to the easy connection between the quantities which are measured in the experiments, like the scattering intensity pattern or the intensity autocorrelation function, and those predicted by statistical mechanics, like the density fluctuations in time and space. This usually allows immediate testing of theories and models without referring to complicated models in the interpretation of the experimental data. This last statement however is based on the assumption that our scattering experiment can be considered as *ideal*: in general we assume that such a scattering experiment is performed in the single scattering regime, the signal is detected in the far field and that all properties are accessible by time averaging. An immediate consequence is that every detection angle can be univocally associated with a particular wave vector transferred during the scattering process. For the majority of colloidal systems of interest however these ideal conditions turn out to be too stringent and as a consequence complicate or preclude the application of light scattering techniques. Fortunately over the last ten to fifteen years we have seen a surge of activity in the development of experimental schemes that allow to overcome many of these limitations. The purpose of this article is to review some of the most important developments in the field of light scattering techniques applied to colloidal systems.

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2. New methods and instrumentation

2.1. Small angle light scattering

During the last years we observed a rapid development of small angle scattering techniques (SALS). This development is essentially related to the progress in charge-coupled device (CCD) sensor technology and to the increasing interest in the study of systems inhomogeneous on length scales of the order or larger than the wavelength of light. Modern devices can cover a range of scattering vectors typically 2×10^{2}–2×10^{4} cm^{-1} which for visible light corresponds to angles of ≈ 0.01–$10°$. Systems with structural properties on these length scales of $2\pi q^{-1}\approx 3$–300 μm include for example colloidal aggregates, gels and glasses, systems undergoing a spinodal decomposition, critical systems, polymer blends, emulsions, foams, red blood cells, vesicles. It is also worth mentioning that SALS has immediate applications to the problem of particle sizing for practical and industrial applications like environmental pollution monitoring. Performing experimental SALS measurements is not easy because in the forward direction one must deal with the strong transmitted beam and with the unavoidable stray light. A recent successful layout proposed to perform low-angle scattering experiments makes use of a peculiar optical scheme to get rid of these difficulties. The light emerging from the sample (transmitted + scattered light) is collected by a lens placed immediately after the sample. It is known from Fourier Optics that the far field intensity distribution $I(q)$ of the light scattered from the sample appears in the focal plane of this lens together with the diffraction spot of the transmitted beam. This latter is much more intense than the scattered light and must be disposed of by using a beam stop accurately positioned in the focal plane. An image of this plane is then formed onto the CCD sensor which collects a 2D projection of the scattered intensity. The limitations imposed by stray light on SALS measurements can be attenuated by carefully subtracting a background signal obtained by filling the experimental cell with the pure solvent. By using this subtraction scheme quantitative static and dynamic light scattering experiments in the q range between 200 cm^{-1} and 20000 cm^{-1} have been performed [1,2••,3•,4–6].

2.2. Near-field scattering

A major innovation in the field of low-angle scattering instrumentation is represented by the family of near-field scattering (NFS) techniques, recently introduced by the group of M. Giglio in Milan [7••,8•,9]. In contrast to traditional SALS techniques the scattered light is not collected in the far field of the sample but very near to it. The experimental setup is quite simple. A large collimated beam impinges on a parallelepiped cell containing the sample. The intensity distribution in a plane at a very small distance z from the sample is directly collected by a CCD sensor. Equivalently a (de)magnified image of the same plane is formed on the CCD sensor by using a lens with a sufficiently high numerical aperture. This intensity distribution has the typical shape of a speckle field but, at variance with the case of far field speckles, the speckle size does not change with z and quite remarkably can be shown to coincide with the size of the scatterers. The intensity distribution $I(q)$ can be derived by Fourier analysis of the speckle images. The NFS technique can be realized by using two very different conceptual schemes: (i) a homodyne NFS [7••], where the strong transmitted beam is removed in the focal plane of the imaging lens by using a beam stop; (ii) a heterodyne NFS [8•] where the interference between the weak scattered light and the strong transmitted beam is exploited. Although the homodyne version was the first to be introduced, the heterodyne scheme offers many advantages and is the layout preferred in practice. Its intrinsic self-referencing nature is the main benefit compared to the homodyne layout. The intensity distribution collected by the CCD sensor is due to the beating between the strong transmitted beam (local oscillator) and the weak scattered light. This implies three very important advantages over traditional light scattering setups (see Ref. [10] for details) First, it guarantees a higher sensitivity as shown in Fig. 1. Second, it allows to measure absolute scattering cross sections without the need of any measurement performed on reference samples. Last, it offers a rather simple way of accurate stray light subtraction without filling the cell with the pure solvent.

It is worth pointing out that the low-q regime of heterodyne NFS coincides with the so-called quantitative shadowgraph [11], used to study the intensity scattered at low angle by non-equilibrium systems [12,13]. In this regime however the technique suffers from the presence of a q-dependent oscillating transfer function which must be taken into account to obtain quantitative data. This transfer function can be disposed of also at low q by using another variant of the NFS technique which is based on Schlieren filtering of the intensity distribution [9]. The lowest q accessible to NFS technique roughly corresponds to the size of the region imaged on the CCD sensor which is of the order of 10 cm^{-1}. As a last remark it is appropriate to point out that these incredibly low wavevectors can be accessed only because in the heterodyne NFS configuration the measurements are performed "inside" the transmitted beam, instead of removing it by using beam-stops like in the usual far field layouts. Very recently also the possibility of exploiting NFS like techniques for dynamics measurements has been pointed out [14•].

2.3. Cross-correlation techniques — multiple scattering suppression

To characterize the structural properties of macroscopically homogeneous soft materials, such as colloidal, polymeric or micellar systems information on the relevant mesoscopic length scales is needed, spanning from 100 nm to several microns. Such information is often obtained from traditional light scattering goniometers that monitor singly scattered visible light over

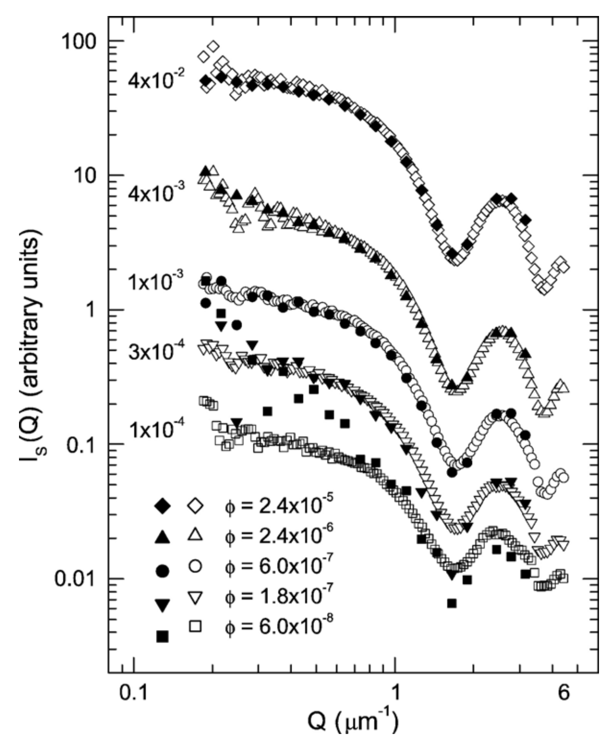

Fig. 1. Comparison between the scattered intensity distributions recovered by the heterodyne near-field scattering (HNFS) technique (open symbols) and by a state of the art low-angle light scattering (LALS) apparatus (solid symbols). The sample under study is a solution of 3 μm diameter latex particles at different volume fractions. The number by each data set indicates the expected beam attenuation. Figure reprinted with permission from Ref. [10]. Copyright (2004) by the American Physical Society.

scattering angles 10°–150°. In the past the application of these methods has been complicated by presence of multiple scattering contributions. Already at moderate densities the scattering length can become smaller than the sample size, in particular for systems based on colloidal particles. Whereas in SALS it is possible to confine the sample to a rather thin film [15] and thus reduce multiple scattering, this is generally not possible in a goniometer setup that requires cylindrical cells of minimal diameter of (several) mm. To maximally reduce the photons path lengths one can use fiber optical probes [16,17] directly immersed in the (liquid) sample. This approach known as Fiber Optical Quasi Elastic Light Scattering (FOQELS) has been applied in a number of studies (e.g. [18]). The application of FOQELS is however limited to backscattering angles around 180° and moreover the interpretation of the data is often complicated due to the incomplete suppression of multiple scattering. Rather than using small scattering volumes it has been shown by Schatztel that it is actually possible to *filter* out singly scattered light and thus suppress contributions from multiple scattering [19]. During the last decade a number of different theoretical and experimental approaches to this problem have appeared [20]. The general idea is to isolate singly scattered light and suppress undesired contributions from multiple scattering in a dynamic light scattering (DLS) experiment. This can be achieved by performing two scattering experiments simultaneously on the same scattering volume (with two laser beams, initial wave vectors $\mathbf{k}_{i1}$ and $\mathbf{k}_{i2}$, and two detectors positioned at final wave vectors $\mathbf{k}_{f1}$ and $\mathbf{k}_{f2}$) and cross-correlating the signals seen by the two detectors. If both experiments then have exactly the same scattering vector $\mathbf{q}$ (i.e., both in magnitude as well as in direction), but use different scattering geometries, each detector sees exactly the same spatial Fourier component of the sample. Schatztel [19] and his collaborators successfully implemented the two-colour method (TCDLS) [21]. While this method has been demonstrated to work by several groups (see [20] and Refs. therein), it is technically extremely demanding and requires sophisticated alignment procedures. The so-called 3D cross-correlation experiment (3DDLS) is technically much less demanding since it works in a similar way than traditional goniometer devices. Instead of a single incident beam now two incident and two detected light paths are placed at an angle $\delta/2$ above and below the plane of symmetry of the scattering experiment. This scheme suppresses contributions from multiple scattering by several orders of magnitude and can still be used like traditional light scattering apparatus [20,22•,23•,24•].

Another cross-correlation approach to suppress contributions of multiple scattering is based on a single-beam two-detector configuration [25•,26,27•]. Suppression of multiple scattering in this configuration is a consequence of the van Cittert–Zernike theorem [27•], which states that intensity correlations in an observation region are closely related to the Fourier transform of the intensity distribution across the source. This means that a small region of single scattering (e.g. the volume of a focused beam) will produce large correlated areas (speckles), whereas a comparably large halo of multiple scattered photons will give rise to small speckles. If two detectors are placed at a distance larger than a multiple scattering speckle but smaller than a single scattering one, by cross-correlating the detectors output it is possible to reduce the effect of multiple scattering. A successful implementation of this approach has been demonstrated by Meyer et al. [25•] by using two spatially separated optical fiber detectors and later by Zakharov et al. by using an area detector [27•]. It has been shown that the suppression ratio can be tuned by choosing a larger separation albeit at the cost of a decreased signal. Choosing a large distance on the other hand might prove unnecessary for small amounts of multiple scattering. It is due to these practical difficulties, that the technically simpler single-beam cross-correlation geometry is often considered inferior to the two-beam realization where a sample independent accurate theoretical description is available.

2.4. Opaque systems and diffuse light analysis

In many dense systems scattering is so strong that no single scattered light is transmitted and in this regime even the previously mentioned approaches fail. The light propagation can be modelled as a diffusion process with light being scattered in random directions thus smearing out the q-dependence of scattering. In the absence of absorption the scattering properties are now characterized by the transport cross section σ^* which for colloidal particles can be derived from Mie-theory. The diffuse transmission coefficient for a slab of thickness L is given by $T \approx l^*/L$ where $l^* \propto 1/\sigma^*$ denotes the transport mean free path. Information about structural order or particle sizes in this regime is therefore only accessible in an indirect way by comparison of l^* with Mie-theory and structure modelling. The l^* parameter can be extracted both from transmission [28•] and backscattering experiments [29]. A more refined method to determine the scattering properties in opaque media is frequency domain photon migration (FDPM). It allows to determine the absorption and isotropic scattering properties separately with high precision and accuracy by modulating the laser beam intensity (for details see [30]).

In principle model independent q-resolved information can be recovered if the wavelength dependent transmission is analyzed. This approach has been named diffuse transmission spectroscopy (DTS)[28•]. It exploits the fact that the maximum momentum transfer $q_{\max} = 2\,k_0$ is wavelength dependent. In turn the wavelength dependence of l^* can be related to the q-dependence of the scattering cross section or $I(q)$. In practice the method suffers however a number of limitations. The transmission coefficient T can only be recorded over a limited range of wavelengths, the wavelength dependent refractive index of the sample has to be known, the sample must be in the diffusive regime for all wavelengths and the accuracy of the measurement itself is rather limited.

The analysis of intensity fluctuations in the multiple scattering regime is known as *Diffusing Wave Spectroscopy* (DWS). Originally introduced already in 1987 [31,32] the technique has steadily gained popularity among users. The experimental setup is relatively simple and it provides accurate information about local displacements in highly turbid media. Compared to standard DLS, DWS even offers some particular advantages. In standard DLS experiments the fluctuations of light are due to single scattering events and displacements of the order of the wavelength can be resolved, typically in the 100 nm range. DWS works in the opposite regime. Due to the long multiple scattering path in the medium the photon undergoes a large number N of scattering events. If each object moves a small distance the cumulative phase shift of all objects along a path is enough to de-phase the scattered light completely. This implies that very small displacements, of the order of $\lambda/\sqrt{N}$ are sufficient to induce light fluctuations. Typical values for $\lambda/\sqrt{N}$ can lie in the sub-nanometer range and this makes DWS a much more sensitive probe as compared to DLS. This advantage of DWS plays an important role when using light scattering for the analysis of dynamic properties of dense viscoelastic solids such as glasses and gels.

The new experimental schemes we will discuss in a following section provide rapid and convenient access to correlation times over many orders of magnitude from 10^{-8}–10 s and more. Now that these new experimental techniques are available DWS can be used in its most efficient way.

2.5. Low coherence scattering

Early experiments in light scattering were performed well before the invention of the LASER in 1960. LASER sources are currently used because of some very desirable properties, the most important being their extremely high brightness. During the last years high brightness broadband sources like light emitting diodes (LED), superluminescent diodes (SLD) and table-top femtosecond light sources have become widely available. Consequently a large number of techniques has been developed which makes use of broadband light sources to investigate weakly and strongly scattering media. All these techniques are based on a very simple idea: interference between two light beams, usually a reference beam and the scattered light, can write stable interference fringes only if the pathlength difference between the two beams is less than the longitudinal coherence length $l_c = \lambda^2/\Delta\lambda$. Here $\Delta\lambda$ is the spread around the central wavelength λ. SLD with l_c of about of 20–30 μm can be easily found in the market and this contributed to the rapid development of an entire field which is known with the name of low coherence interferometry (LCI) [33]. One of the most common layouts is the low coherence Michelson interferometer which allows to perform depth resolved scattering studies of scattering samples with a depth spatial resolution of the order of l_c. This layout is used for example in the so-called Optical Coherence Tomography (OCT) [34], which offers penetrations in the sample under study of the order of 2 cm in weak scattering condition and 1–2 mm in strongly scattering systems. For this reason OCT is widely used in medicine for biological tissue investigation. Low coherence light sources can also be profitably used for the study of dynamic processes [35•,36•]. This is true especially for those systems which cannot be studied with DLS or DWS because they are neither single nor strongly multiple scattering. In traditional DWS experiments the data reduction requires assumptions on the statistics of photon paths in the medium. If the system exhibits strong multiple scattering a diffusive model for the photon works very well. As the sample scattering decreases this model can be violated and reasonable assumptions on the pathlength distribution must be made. An alternative approach to the problem has been provided by Dogariu and Popescu at least in a backscattering geometry [33]. The photon pathlength distribution can be measured directly by using a technique called Optical Pathlength Spectroscopy (OPS). This technique is based on the LCI scheme in the Michelson configuration. By virtue of the limited temporal coherence of the light source it is possible to isolate optical paths of length s with a resolution equal to l_c. By performing a scan with the reference mirror it is therefore possible to reconstruct the photon pathlength distribution which can be used to analyze DWS data. It is clear that also in this case the main limiting factor is the penetration length in the sample. The light traveling long paths in the sample can be strongly attenuated and the characterization of the tails of the pathlength distribution can become difficult.

3. Multi-speckle dynamic light scattering — slow relaxations and arrested dynamics

In solid-like media, the scatterers are localized near fixed average positions, probing only a small fraction of their possible spatial configurations by thermal motion. As a consequence, the measured time-averaged quantities (such as the scattered intensity or its autocorrelation function) differ from the ensemble-averaged ones [37–41•]. The non-fluctuating part of the scattered electric field amplitude acts as a local oscillator. The level of heterodyning however can vary depending on the sample configuration. Since the field amplitudes interfere on the detector a simple rescaling or shifting of the intensity correlation function is not possible. Pusey and van Megen showed in 1989 how to correctly normalize the measured ICF if the ratio of the field amplitudes can be determined independently, e.g. by a fast rotation of the sample [37]. Their method however works only if the sample is completely arrested and does not display any slow fluctuations on the timescale of an experiment. In practice this requirement is frequently not met, in particular for the very sensitive DWS technique. A number of new powerful tools nowadays provide access to this important slow relaxation dynamics. In this section we want to highlight the most important improvements that have been reported over the last decade.

3.1. Dynamic light scattering using a multi-pixel detector

It has been demonstrated by Kirsch et al. that a video camera based area detector can be used in a standard goniometer based light scattering equipment to study slow relaxations in colloidal systems such as hard sphere glasses [42••]. For low-angle scattering setups a very distinctive feature discussed in Section 2.1 is that, by careful design of the optics, the speckle size on the sensor can be matched with the pixel size [3•]. In this way the CCD sensor becomes equivalent to a large (of the order of 10^6) ensemble of intensity autocorrelators working in parallel. For most systems the scattering pattern has azimuthal invariance and it is possible to operate a multi-speckle scheme where an ensemble average of the autocorrelation function can be calculated without the need of any rotation or translation of the sample under study [42••,45•]. It is worthwhile to note that for typical multi-speckle DWS implementations all pixels can be treated equally which represents a huge speckle ensemble and in turn leads to high quality data.

It is clear that the main limitation of this CCD DLS scheme is related to the limited frame rate of standard CCD cameras (currently of the order of 0.1–1 kHz) which is not yet comparable with the fast hardware autocorrelator (up to 100 MHz). Also the detection efficiency of the CCD sensor is often lower as compared to modern single mode fiber and photon counter combinations, thus requiring a higher laser power when using fast cameras. Nevertheless for small angle scattering applications the time resolution is usually sufficient. However for large scattering angles or DWS applications the fluctuations are faster. In this case CCD multi-speckle detection has to be combined with traditional photon correlation spectroscopy if the full range of correlation times needs to be measured [44,43,46].

It is worthwhile to mention here a different approach that does not attempt to reveal all details of the intensity autocorrelation function. The speckle visibility spectroscopy (SVS) approach introduced by Durian and co-workers analyzes the speckle contrast (standard deviation of the intensity distribution) of a single CCD image taken with a certain exposure time T [47•]. In the case the system has substantially evolved, or rearranged, during the time T the speckle pattern will be blurred and in turn the contrast reduced. For the case of Gaussian fluctuations the speckle contrast can be expressed as a triangular average of the intensity correlation function. The contrast is thus an integrated measure of the sample dynamics on time scales shorter than T. The main advantage of the method is its relatively high temporal resolution and its simplicity. Using a fast video camera and a strong laser values of T of 50 μs can be achieved. It is worthwhile to note that in a different field of research, biomedical imaging, a very similar technique is known since the early 1980's under the name of laser speckle imaging (LSI) or laser speckle contrast analysis (LASCA) [49,48].

3.2. Multi-speckle averaging with echo techniques

A different approach to multi-speckle dynamic light scattering in DLS has been introduced by Pham et al. using a so-called echo technique [50••]. If the cylindrical sample is rotated at a constant frequency f correlation peaks appear at each revolution. The peak height and area were shown to be a measure for the ensemble averaged correlation function [50••]. The main advantage of the method is that it can be easily implemented in existing scattering setups. Therefore static light scattering data and DLS at short times can be obtained using the same sample. It is worthwhile to note that this new echo DLS technique is conceptually similar to the interleaved sampling method developed previously [51]. The echo scheme however is based on much more efficient signal processing which makes it a powerful tool in routine analysis.

Echo–DWS was initially introduced in the analysis of non-linear shear deformation [52•,53]. If the sample deformation is completely reversible under shear the DWS correlation function displays correlation peaks of equal height. Relaxation of the microstructure leads to a loss of correlation between shear cycles.

Zakharov et al. recently demonstrated that multi-speckle echoes in DWS can also be recorded in a two cell geometry [54•]. In contrast to previous echo experiments in this case the sample is at rest which allows higher rotation frequencies. If combined with the previously reported two-cell DWS technique (TCDWS) [41•] correlation times from 10 ns up to duration of measurement can be accessed almost in real time. Again the main advantage compared to the (somewhat more accurate) CCD sensors is the fact that both fast and slow relaxations can be recorded with the same experimental setup.

3.3. Monitoring intermittent dynamics

Traditional dynamic light scattering provides time averaged information about the dynamic structure factor. The method therefore implicitly assumes that the dynamic properties are stationary and intensity fluctuations are Gaussian.

In other words correlating a pair of speckle patterns separated by a delay time τ should always result in the same correlation coefficient independent of the time the experiment is done. This is obviously not the case for gradually evolving systems as encountered for example in a gelation process. If however the process is slow the evolution is quasi-stationary and the intensity correlation function remains a good quantity to characterize the system.

The situation is qualitatively different in systems such as granular media, foams or many glassy materials. Such systems do not evolve continuously but are often characterized by sudden intermittent changes. Intermittent events however are not revealed by recording the time averaged intensity correlation function $g^{(2)}(\tau)$. High order correlation functions, in fact contain information about non-stationary dynamics as shown by Lemieux and Durian [55•]. In contrast to $g^{(2)}(\tau)$ the fourth order correlation function $g^{(4)}(\tau)$ can distinguish between intermittent and continuous dynamics. A successful implementation of this approach has been reported by monitoring the intermittent dynamics in sand piles [56]. Since the method requires time averaging $g^{(4)}(\tau)$ it cannot be applied to very slow or non-stationary processes.

The more powerful approach TRC of Cipelletti et al. overcomes this difficulties, again by using an area detector. The so-called time resolved correlation (TRC) method determines the correlation coefficient $c(t, \tau)$ by multiplying two far-field speckle images taken at time t and $t+\tau$ without any need for further time averaging [57••]. It is now possible to monitor the *amount* of correlation $c(t, \tau)$ as a function of correlation time τ, as it is done in a traditional experiment, or as a function of t. The latter case is the most interesting one. In a system with Gaussian dynamics $c(t, \tau)$ is independent of t within the statistical accuracy of the experiment [58]. In the presence of intermittent events however $c(t, \tau)$ will fluctuate. It has been shown for different systems that sudden events, such as rearrangements of bubbles in a foam structure or stress relaxations in a colloidal gel, can be observed as sudden drops of the correlation coefficient

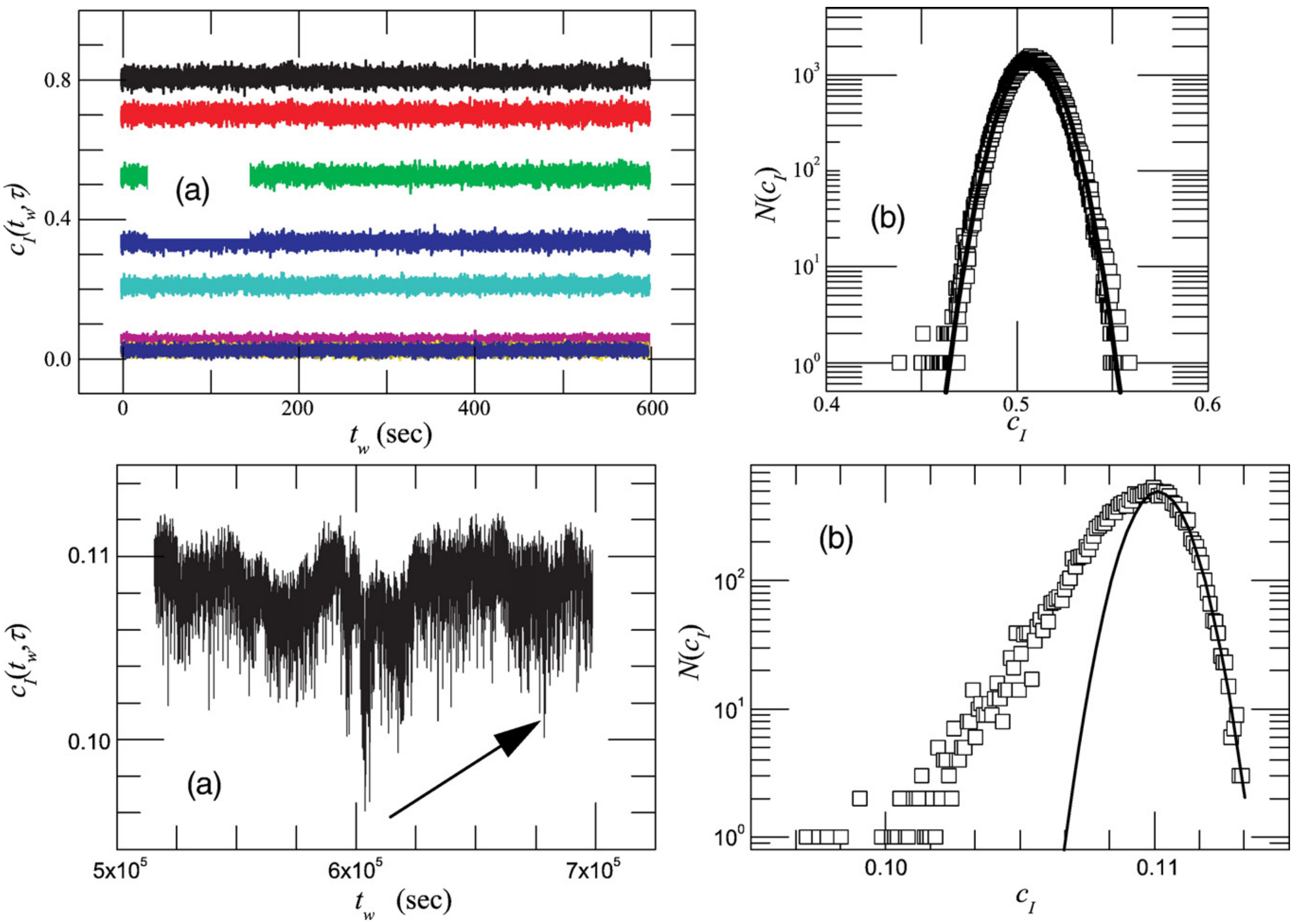

Fig. 2. Above: (a)TRC data for a Brownian sample; from top to bottom, τ is 0.02, 0.04, 0.08, 0.14, 0.2, 0.4, 0.8, 1.4 and 2.0 s. (b) The frequency plot $N(C_I)$ of $C_I(t_w, \tau=0.08$ s) (squares). The curve is a Gaussian fit to the data. Below: (a) TRC data for a colloidal gel at $\Phi=4.5\%$, for $\tau=2000$ s. The arrow indicates one of the sudden, anomalously large losses of correlation. (b) The frequency plot $N(C_I)$ of the data shown in (a). The curve is a Gaussian obtained by fitting the data to the right of the maximum of $N(C_I)$. Figure reprinted with permission from Ref. [57••]. Copyright (2003) by IOP Publishing Ltd.

[57••,59]. This type of behavior would go completely unrecognized in a classical time-averaged experiment. The fluctuations of the correlation coefficient itself can serve as a measure of the amount of dynamic heterogeneities. In Fig. 2 we reproduce from Ref. [57••] TRC data for a Brownian sample (above) and for a colloidal gel (bottom). The correlation coefficient $c(t, \tau)$ for the Brownian motion (first column) evolves with time in a very regular way and the frequency plot (second column) of $c(t, \tau)$ for fixed τ is symmetric around the peak value. By contrast the gel dynamics has a very intermittent behaviour and a strongly asymmetric frequency plot. These quantities in turn can be linked to theoretical models for example in glass forming systems [59]. TRC thus opens a completely new window to study dynamic properties in soft materials.

4. Conclusions

We have seen that progress in instrumentation and new experimental approaches nowadays provide a set of powerful tools to study colloidal systems using visible light as a probe. The new trends in light scattering allow to extend the limits and thus allow to target new applications such as the structural analysis of large scale heterogeneities or the study of relaxations in soft glassy materials. Many of the new techniques provide improved data quality and allow reduced measurement times. The kind of improvements and new schemes highlighted in this article guarantee that light scattering will remain one of the most important techniques in the analysis of colloidal systems.

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